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Chemical Structure and Surface Activity

VIII. Statistical Evaluation of the Influence of Alkyl Monoethers of Polyoxyethylene Glycols Structure on Their Adsorption at the Aqueous Solution–Air Interface

ADAM SOKOŁOWSKI AND BOGDAN BURCZYK

Institute of Organic and Polymer Technology, Technical University of Wrocław, 50-370 Wrocław, Poland

Surface tension isotherms of the individual alkyl monoethers of polyoxyethylene glycols $C_nH_{2n+1}(OCH_2CH_2)_zOH$ (n from 4 to 8; z from 1 to 5) at the aqueous solution–air interface have been determined. By using the appropriate multiple regression equations a quantitative correlation has been found between the change of standard free energy of adsorption, ΔG°, and the structure of the studied monoethers and of aliphatic alcohols as well. It has been found that within the studied range of surface tension decrease, π from 0 to 20 mN m^{-1}, the change of standard free energy of adsorption, ΔG°, for the monoethers cannot be regarded as a sum of increments $\Delta G^\circ[X_i]$ corresponding to the definite fragments, X_i, of monoether molecules. It has been shown, that not only methylene groups, $-CH_2-$, of the hydrocarbon chain, but the $-OCH_2CH_2-$ groups of the polyoxyethylene chain have the hydrophobic character as well. The interaction of both these fragments is statistically significant and has an influence on the total value of ΔG°. However, the hydrophobic character of the $-OCH_2CH_2-$ grouping is not constant. For the group of compounds studied it decreases with the increasing length of hydrocarbon chain and with an increase in π. For example, for $\pi = 20$ mN m^{-1}, $\Delta G^\circ[-OCH_2CH_2-]$ for the series of butyl and octyl derivatives is -0.32 and -0.13 RT, respectively. By assuming a simplified additive model which has been most often used to describe the relationships between ΔG° values and the chemical structure of surfactants at interfaces, we have calculated the $\Delta G^\circ_{\pi-20}[-CH_2-]$ and $\Delta G^\circ_{\pi-20}[-OCH_2CH_2-]$ values for the monoethers using multiple regression equations. These values are -1.07 and -0.25 RT, respectively. The $\Delta G^\circ_{\pi-20}[-CH_2-]$ value for aliphatic alcohols is -1.29 RT. By comparing the increments $\Delta G^\circ_{\pi-20}[-OH]$ for monoethers and alcohols ($\Delta\Delta G^\circ_{\pi-20}[-OH] = -0.5$ RT) it can be seen that the $-OH$ group at the end of the polyoxyethylene chain seems to be less hydrated in the adsorption layer. This is probably caused by the participation of the mentioned hydroxyl group in inter- and intramolecular hydrogen bonds.

INTRODUCTION

In the past several years a number of works have been devoted to studies on the quantitative description of the relationship between adsorption of surfactants at the interfaces and their structure (1–9). One of the often used, measures of adsorption is standard free energy of adsorption, ΔG°. On determining it, it is assumed usually that the individual groupings of the molecule have an additive contribution to the determined ΔG° value of the compound. In the case of surfactants with a simple bipolar structure, $CH_3(CH_2)_{n-1}W$, where W is a hydrophilic group, Rosen (1, 2) has separated $\Delta G^\circ_{\pi-20}$, i.e., the ΔG° value calculated for a surface tension decrease $\pi = 20$ mN m^{-1} into three components, $\Delta G^\circ_{\pi-20}[X_i]$, according to Eq. [1]:

$$\Delta G^\circ_{\pi=20} = \Delta G^\circ_{\pi=20}[CH_3-] + (n-1)$$

$$\times \Delta G^\circ_{\pi=20}[-CH_2-] + \Delta G^\circ_{\pi=20}[-W] \quad [1]$$

where the $\Delta G^\circ_{\pi-20}[CH_3-]$, $\Delta G^\circ_{\pi-20}[-CH_2-]$, and $\Delta G^\circ_{\pi-20}[-W]$ values are related to the energy of transfer of, respectively, the methyl end group, the methylene group in hydrocarbon chain, and the hydrophilic group, from the aqueous phase to the interface.

369

370   SOKOLOWSKI AND BURCZYK

A similar approach is used on determining the value of standard free energy of micellization (10, 11).

Oxyethylene derivatives of aliphatic alcohols are thought of as an example of nonionic surfactants, in which a polyoxyethylene group has an unequivocal hydrophilic character (12). In such compounds having the general formula $C_nH_{2n+1}(OCH_2CH_2)_zOH$ there are two groupings with hydrophilic properties which contribute to the total W: a hydroxyl group and an oxyethylene chain, $(-OCH_2CH_2-)_z$. Thus, the structure of these compounds differs fundamentally from that of simple, bipolar compounds, for example, aliphatic alcohols, monocarboxylic acids and their salts, alkyl sulfates etc. It may be expected that the presence of a polyoxyethylene chain of varying length between an alkyl chain and a hydroxyl group of a small volume can have a varying influence on the adsorption of compounds containing this grouping. Some suggestions confirming this assumption can be found in the data reported by Crook et al. (8) concerning adsorption of oxyethylene derivatives of p-t-octylphenol at the aqueous solution–air interface. Our attention was called to the fact that $\Delta G^\circ_{\pi=20}$ attains increasingly negative values with the increasing number of oxyethylene groups within the range, z from 1 to 4. This seems to suggest a hydrophobic character of the $-OCH_2CH_2-$ group, and only at considerably higher values of z an opposite change in the $\Delta G^\circ_{\pi=20}$ values was observed. An apparently hydrophobic character of this group was found for ionic surfactants, e.g., ether alcohol sulfates (12, 13). However, reasons given by Lange et al. to explain the hydrophobic properties of the $-OCH_2CH_2-$ group cannot be applied directly to oxyethylenated alcohols.

We could not find any systematic studies on the function of the $-CH_2-$, $-OCH_2-CH_2-$, and $-OH$ groups in nonionic surfactants depending on their surface tension decrease. Rosen has reported the data on adsorption of surfactants at the aqueous solution–air interface, but these results have

been obtained for the constant value of the surface tension decrement of 20 mN m^{-1}, for which the coverage of the surface for a majority of surfactants is from 84 to 99.9% (1, 2).

Moreover, a majority of the authors have determined the mentioned increments graphically by estimating separately the contribution of oxyethylene groups at a constant alkyl radical, or the contribution of the $-CH_2-$ group in different alkyl groups for a constant length of the polyoxyethylene chain. Such a procedure omitting the need for the parallel estimation of the increments $\Delta G^\circ[X_i]$ can give inaccurate numerical values.

In the present work we attempt to give a quantitative relationship between ΔG°_π and structure of some nonionic surfactants in the form of a mathematical model. At present our discussion will be limited only to alkyl monoethers of polyoxyethylene glycols (I) and, for comparison, aliphatic alcohols (II)

$$C_nH_{2n+1}(OCH_2CH_2)_xOH \qquad C_nH_{2n+1}OH$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
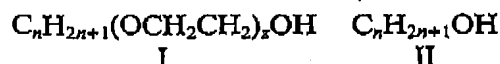
By choosing the appropriate equations, we aimed at (i) the statistical verification of the additive approach expressed by Eq. [1], by taking into account oxyethylene groups contribution and finding possible contributions of statistically significant interactions between particular fragments of a molecule to the total value of $\Delta G^\circ_{\pi=const.}$; (ii) comparing the values of increments $\Delta G^\circ_{\pi=const.}[X_i]$ ascribed to the same fragments of molecules of compounds (I) and (II); and (iii) proposing a mathematical model which would make it possible to predict the course of surface tension isotherm for aqueous solutions of these compounds within a broad range of coverage at the aqueous solution–air interface.

MATERIALS AND METHODS

Materials. Individual n-butyl, n-amyl, n-hexyl, n-heptyl, and n-octyl monoethers of polyoxyethylene glycols containing from 1 to 5 oxyethylene units per molecule were

ENERGY OF ADSORPTION OF NONIONICS   371

obtained by the fractional distillation of a polydisperse mixture obtained in the addition reaction of ethylene oxide to the corresponding aliphatic alcohols (14). The purity of isolated ethers as determined by means of gas–liquid chromatography (stationary phases: Apiezon APZL (15%) on Chromosorb Q and Carbowax 20 M (10%) on Chromosorb G/AW DMCS) was greater than 99%. The compounds obtained are colorless liquids. In Table I some physical properties of these substances are listed.

Surface tension measurements. Surface tension of aqueous solutions of monoethers (I) was determined by the maximum bubble pressure method at $293.2 \pm 0.2°K$. In separate experiments the time necessary for the

TABLE I

Physical Properties of Individual Monoethers of Polyoxyethylene Glycols

Structure of compounds				
n	z	d_{4}^{293}	n_{D}^{293}	bp (°K/mm Hg)
4	1	0.9039	1.4196	342–344/11
4	2	0.9555	1.4320	378/6–8
4	3	0.9865	1.4396	418–418.5/8
4	4	1.0104	1.4455	437–439/5.5
4	5	1.0314	1.4491	465/2
5	1	0.9003	1.4249	348.5–349/8
5	2	0.9434	1.4348	391/7
5	3	0.9734	1.4412	415–419/5–6
5	4	0.9994	1.4461	447–450/3
5	5	1.0200	1.4500	466/1
6	1	0.8879	1.4290	362–366/5–6
6	2	0.9395	1.4375	404–405.5/5
6	3	0.9680	1.4430	426–428/5
6	4	0.9882	1.4466	458/3.5
6	5	1.0093	1.4505	480–483/2
7	1	0.8864	1.4327	380–381/12
7	2	0.9274	1.4394	397–399/4.5
7	3	0.9573	1.4442	429/4.5
7	4	0.9818	1.4485	458/1
8	1	0.8827	1.4361	395–395.5/8
8	2	0.9228	1.4419	416–418/5.5
8	3	0.9528	1.4460	443–447/2
8	4	0.9734	1.4495	474–475/2

generation of the gas bubble to reach equilibrium conditions was determined. Surface tension values for aqueous alcohol (II) solutions at 298.2°K were taken from the work of Posner *et al.* (15). These authors determined surface tension of aqueous solutions of *n*-butanol by the maximum bubble pressure method, and in the case of aqueous solutions of *n*-pentanol, *n*-hexanol, *n*-heptanol, and *n*-octanol by the drop volume method.

RESULTS AND DISCUSSION

We have determined surface tension isotherms of aqueous solutions of monoethers (I) containing a varying number of methylene and oxyethylene groups in their hydrophobic and hydrophilic parts. The studied compounds were characterized by a moderate surface activity. The relationship between surface tension and the concentration of monoether (I) containing four ($z = 4$) oxyethylene groups ($-OCH_2CH_2-$) per molecule is shown in Fig. 1. All the monoethers studied, except for butyl ether of tetraethylene glycol, exhibit CMC. However, none of the γ-log c curves indicated any dip in the vicinity of the CMC.

We have found that the experimental values of surface tension are described well by the Temkin isotherm (16) in the integral form:

$$\ln B + \ln x = g \cdot \pi^{1/2}/RT. \qquad [2]$$

where g is a constant, x is the molar fraction of the monomer at a constant value of surface tension decrement π [mN m^{-1}], and B is the equilibrium constant of the adsorption process. By plotting the values of $\pi^{1/2}$ vs $\ln x$ a linear relationship has been obtained (Fig. 2). Through extrapolation of the straight lines to $\pi = 0$ we have determined the extrapolated value of $\Delta G°$:

$$\Delta G°_{\pi \to 0} = -RT \ln B = RT \ln x_{\pi \to 0}. \qquad [3]$$

The standard states were assumed as follows: $\pi = 1$ mN m^{-1} for the surface, and a hypothetical state in which the product of mole fraction and activity coefficient is unity, for
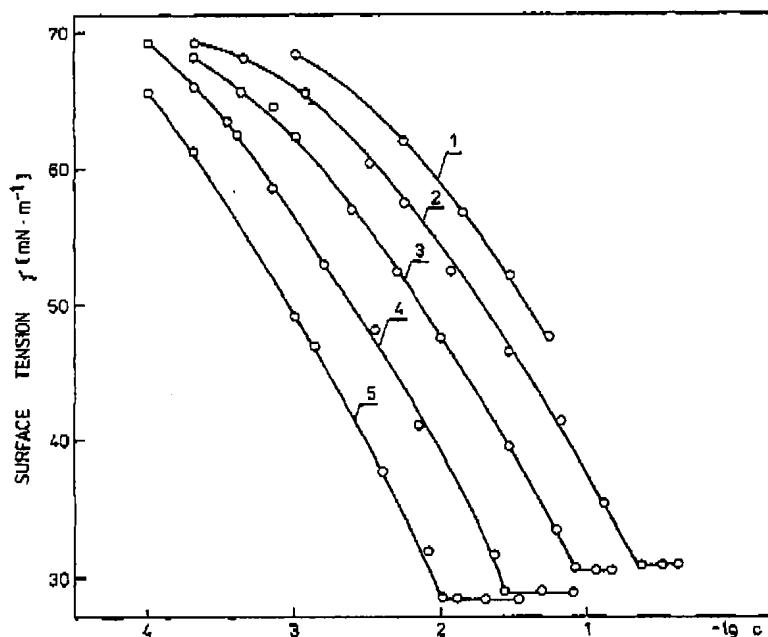
372   SOKOLOWSKI AND BURCZYK

FIG. 1. Relationship between surface tension, γ, and concentration of aqueous solutions of alkyl monoethers of tetraoxyethylene glycol. (1) Butyl, (2) amyl, (3) hexyl, (4) heptyl, and (5) octyl ether.

the solution. The constants of the Temkin isotherm are shown in Table II.

In order to find the quantitative relationship between the adsorption of monoethers (I) and their structure, we calculated the regression equation
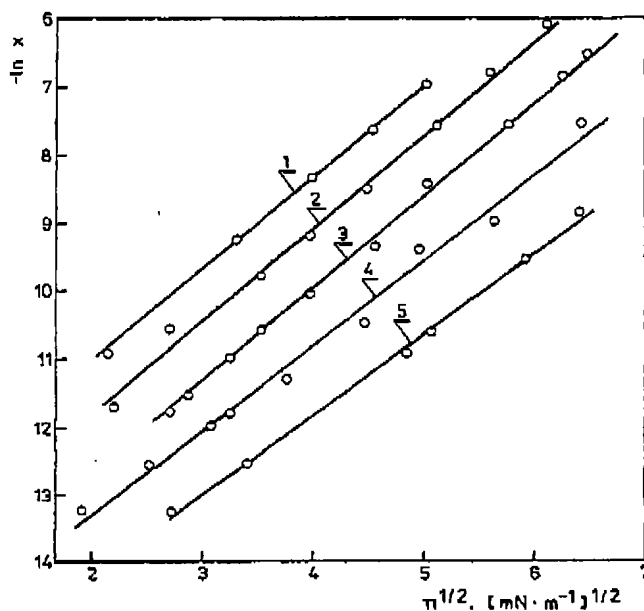

FIG. 2. Relationship of ln x = $f(\pi^{1/2})$ obtained for (1) butyl, (2) amyl, (3) hexyl, (4) heptyl, and (5) octyl ether of tetraoxyethylene glycol.

ENERGY OF ADSORPTION OF NONIONICS   373

TABLE II

Constants of Temkin Adsorption Equation

Structure of compounds (I) and (II)		$g \cdot 10^{-4}$ [$N^{1/2}$ $m^{1/2}$ mole^{-1}]		ln B	
n	z	detd[a]	calcd[b]	detd[a]	calcd[c]
4	1	8.00	8.22	11.01	11.35
4	2	8.93	9.08	12.07	12.10
4	3	9.66	9.94	12.65	12.84
4	4	10.82	10.80	13.55	13.59
4	5	11.73	11.67	14.57	14.34
5	1	7.87	7.60	12.00	12.06
5	2	8.67	8.47	13.05	12.81
5	3	9.08	9.33	13.50	13.56
5	4	10.07	10.19	14.27	14.31
5	5	11.19	11.05	15.18	15.06
6	1	7.53	6.99	13.01	12.78
6	2	8.25	7.85	13.94	13.53
6	3	8.58	8.71	14.21	14.28
6	4	9.57	9.58	14.87	15.03
6	5	10.61	10.44	15.92	15.78
7	1	6.44	6.38	13.54	13.50
7	2	6.94	7.24	14.18	14.24
7	3	7.75	8.10	14.94	14.99
7	4	9.21	8.96	15.63	15.74
8	1	6.03	5.76	14.45	14.21
8	2	6.23	6.63	14.84	14.96
8	3	6.64	7.49	15.38	15.71
8	4	9.05	8.35	16.49	16.46
4	0[d]	6.36	6.34	9.49	9.55
5	0	6.02	6.08	10.69	10.68
6	0	5.79	5.82	11.82	11.81
7	0	5.74	5.55	13.10	12.94
8	0	5.18	5.29	13.94	14.07

[a] By Eq. [2].

[b] By Eqs. [4a] and [4h] for compounds (I) and (II), respectively.

[c] By Eqs. [4b] and [4i] for compounds (I) and (II), respectively.

[d] Calculations based on the values of surface tension reported by Posner et al. (15), measured at 298°K. The values of surface tension measured by Posner at 285, 298, and 312°K allow one to compare the numerical results obtained from surface tension measurements at 293 and 298°K for aqueous solutions of aliphatic alcohols.

$$Y = b_0 + b_1 \cdot n + b_2 \cdot z + b_3 \cdot n \cdot z, \quad [4]$$

where Y denotes either the constants of the Temkin isotherm equation ($10^{-4} \cdot g$ or $-\ln B$) or the change of ΔG_π^o at constant de-

crease in surface tension, π, in RT units, n is the number of carbon atoms in the hydrocarbon chain, z is the number of oxyethylene units, $-OCH_2CH_2-$, $\pi = \gamma_{H_2O} - \gamma_{solution}$ [mN m^{-1}], and $b_0 \cdots b_3$ are regression coefficients. Equation [4] applied to describe a given Y parameter is referred to as Eq. [4a], [4b], . . . , [4u] as specified below in the text and in Tables III, IV, and VI. The statistical evaluation of the b_j coefficients is presented in the Appendix.

The results of regression analysis of both constants of Temkin's isotherm are listed in Tables III and IV for monoethers (I) (Eqs. [4a] and [4b]) and for alcohols (II) (Eqs. [4h] and [4i]), respectively. In order to verify the calculation procedure, the Temkin's constants were recalculated from b_j values using Eq. [4]. The results are listed in Table II along with the determined constants.

The way in which molecules are oriented at the interface may be concluded from the surface area values, A, occupied by the molecule in the surface layer which, in term, can be determined from the surface excess value, Γ. The Γ values have been determined from the equation of state (16) corresponding to Temkin's isotherm (Eq. [5])

$$\Gamma = \frac{2 \cdot \pi^{1/2}}{g} \quad [5]$$

for a constant decrease in surface tension equal to 20 mN m^{-1} (a monomolecular layer is assumed). The values of Γ and the corresponding surface area values, A, are listed in Table V.

The results of regression analysis of the change of standard free energy of adsorption, $\Delta G_{\pi=const.}^o$ (Eq. [3]), for a series of constant values of the decrease in surface tension until 20 mN m^{-1} are listed in Tables III and IV. The presented values of $\Delta G_{\pi=0}^o$ and $\Delta G_{\pi=1}^o$ are extrapolated ones. The negative values of coefficients b_1 (cf. Tables III and IV) connected with the change of ΔG_π^o per one $-CH_2-$ unit in the hydrocarbon chain, ΔG_π^o [$-CH_2-$], emphasize the hydrophobic character of that chain. Rather high, negative

SOKOLOWSKI AND BURCZYK

TABLE III

Multiple Regressions of the Temkin Isotherm Constants and Values of Standard Free Energy of Adsorption for Monoethers (I) at the Aqueous Solution–Air Interface

Equation: Parameter Y:	[4a] $g \cdot 10^4$	[4b] $-\ln B$	[4c]	[4d]	[4e] ΔG_π°, $[RT]$	[4f]	[4g]
π [mN m^{-1}]:	—	0	1	5	10	15	20
b_0	9.808	−7.049	−5.769	−4.182	−2.982	−2.065	−1.288
$S(b_0)$	(0.385)	(0.379)	(0.310)	(0.251)	(0.238)	(0.243)	(0.278)
b_1	−0.6132	−0.8354	−0.9168	−1.0178	−1.0953	−1.1537	−1.2039
$S(b_1)$	(0.0543)	(0.0631)	(0.0517)	(0.0419)	(0.0396)	(0.0413)	(0.0463)
b_2	0.8621	−0.9968	−0.8891	−0.7563	−0.6596	−0.5856	−0.5215
$S(b_2)$	(0.0564)	(0.1222)	(0.1002)	(0.0812)	(0.0766)	(0.0801)	(0.0896)
b_3	—	0.0439	0.0448	0.0458	0.0471	0.0482	0.0486
$S(b_3)$		(0.0211)	(0.0173)	(0.0140)	(0.0132)	(0.0138)	(0.0155)
$t(b_3)^a$		2.08	2.59	3.27	3.57	3.49	3.14
R	0.977	0.992	0.995	0.997	0.997	0.997	0.997

^{a} $t_{\alpha-0.05} = 2.09$.

values of coefficients b_2 connected with $\Delta G_\pi^\circ[-OCH_2CH_2-]$ (cf. Table III) may seem surprising. It appears that the $(-OCH_2-CH_2-)_z$ groups, thought of as the typical nonionic hydrophilic grouping in nonionic surfactants (12), besides causing an enhancement in the solubility of monoethers, brings about at the same time an increase in hydrophobicity of compounds (I) within the studied range of decrease in surface tension π. This increase in hydrophobicity becomes less apparent with increasing values of π, which is indicated by the b_2 values. We have

found, moreover, that the b_3 also has an influence on the variable Y in all Eqs. [4c]–[4g] (cf. Table III), as indicated by the values of statistics $|t(b_3)| > t_\alpha$. The marked share of the product $b_3 \cdot n \cdot z$ in the total value of $\Delta G_{\pi=const.}^\circ$ of molecule (I) observed at a range of surface tension decrease π from 0 to 20 mN m^{-1} suggests the presence of the interaction between the hydrophobic group C_nH_{2n+1} and the "hydrophilic one" $(-OCH_2CH_2-)_z$. The positive values of the product $b_3 \cdot n \cdot z$ indicate that this interaction has a negative effect on adsorption of mon-

TABLE IV

Regressions of the Temkin Isotherm Constants and Values of the Standard Free Energy of Adsorption for Alcohols (II) at the Aqueous Solution–Air Interface

Equation: Parameter Y:	[4h] $g \cdot 10^4$	[4i] $-\ln B$	[4j]	[4k]	[4l] ΔG_π°, $[RT]$	[4m]	[4n]
π[mN m^{-1}]:	—	0	1	5	10	15	20
b_0	7.402	−5.025	−4.076	−2.913	−2.036	−1.366	−0.773
$S(b_0)$	(0.307)	(0.299)	(0.266)	(0.225)	(0.197)	(0.177)	(0.216)
b_1	−0.2641	−1.1306	−1.1649	−1.2060	−1.2374	−1.2612	−1.2879
$S(b_1)$	(0.049)	(0.048)	(0.043)	(0.036)	(0.032)	(0.029)	(0.035)
R	0.966	0.998	0.998	0.999	0.999	0.999	0.999

Note. $N - K - 1 = 3$; $t_{\alpha-0.05} = 3.18$.

TABLE V

Surface Excess (Γ) and Area per Molecule (A)

Structure of compounds (I) and (II)		$\Gamma \cdot 10^6$ [mole m^{-2}]		$A \cdot 10^{20}$ [m^2]	
n	z	detd[a]	calcd[b]	detd	calcd
4	1	3.53	3.44	47	48
4	2	3.17	3.11	52	53
4	3	2.93	2.84	57	58
4	4	2.61	2.62	63	63
4	5	2.41	2.42	69	69
5	1	3.59	3.72	46	45
5	2	3.26	3.34	51	50
5	3	3.11	3.03	53	55
5	4	2.81	2.78	59	60
5	5	2.53	2.56	65	65
6	1	3.76	4.05	44	41
6	2	3.43	3.60	48	46
6	3	3.30	3.25	50	51
6	4	2.95	2.95	56	56
6	5	2.67	2.71	62	61
7	1	4.39	4.43	38	37
7	2	4.07	3.91	41	42
7	3	3.65	3.49	45	47
7	4	3.07	3.16	54	53
8	1	4.69	4.91	35	34
8	2	4.54	4.27	37	39
8	3	4.26	3.78	39	44
8	4	3.12	3.39	63	49
4	0	4.45	4.45	37	37
5	0	4.70	4.65	35	36
6	0	4.88	4.86	34	34
7	0	4.93	5.09	34	33
8	0	5.46	5.35	33	31

[a] By Eq. [5], $g = g_{detd}$, $\pi = 20$ mN m^{-1}.
[b] By Eq. [5], $g = g_{calcd}$, $\pi = 20$ mN m^{-1}.

oethers (I). The greater the values of n and z, the stronger the mentioned interaction. Moreover the presence of a statistically valid product $b_3 \cdot n \cdot z$ indicates that the value of the increment connected with a $-CH_2-$ group, i.e., $\Delta G^\circ_{\pi=const}[-CH_2-]$, cannot be assigned directly to the b_1 coefficient. Similarly, when evaluating the hydrophobic character of the $-OCH_2CH_2-$ group the values of the following expression—$b_2 \cdot z$ and $b_3 \cdot n \cdot z$—should be taken into account. This may be illustrated by comparing the contribution of the

$-OCH_2CH_2-$ grouping to the total value of ΔG°_π for the two series of compounds: $C_4H_9(OCH_2CH_2)_zOH$ and $C_8H_{17}(OCH_2CH_2)_zOH$. For $\pi = 20$ mN m^{-1}, it follows from Eq. [4g] (cf. Table III):

$C_4H_9(OCH_2CH_2)_zOH$:

$$Y = b_0 + 4b_1 + b_2 \cdot z + 4b_3 \cdot z$$
$$= -6.104 - 0.325 \cdot z \qquad [6]$$

$C_8H_{17}(OCH_2CH_2)_zOH$:

$$Y = b_0 + 8b_1 + b_2 \cdot z + 8b_3 \cdot z$$
$$= -10.92 - 0.129 \cdot z. \qquad [7]$$

Thus, by introducing one grouping $-OCH_2-CH_2-$ into butyl derivatives, their hydrophobic properties are increased by -0.32 RT, but in the octyl ones only by -0.13 RT. This can explain the lack of the hydrophobic contribution by the $-OCH_2CH_2-$ grouping in the typical nonionic surfactants having a hydrocarbon chain longer than C_{10} as reported by numerous authors.

The corroboration of such a negative interaction in oxyethylenated alcohols containing a straight-chain, linear structure, indicates that there is a need to analyze the possibility of the presence of such effects in more complicated surfactants, for example, containing other oxyalkylene units or more than one alkyl chain. The presented approach was applied successfully to determine the effect of the structure of acetals containing three hydrocarbon groupings and two oxyethylene chains, on the change of the ΔG°_π value (17). We have also recalculated the data in Dörfler's work (18) which concerned adsorption of dialkyl phosphine acid alkyl esters at the aqueous solution–mercury interface, to receive the corresponding values of $\Delta G^\circ[X_i]$; unfortunately insufficient experimental data did not allow us to find any possible interactions (17).

As was mentioned earlier, similar interactions have not been taken into account in earlier publications when calculating the increments $\Delta G^\circ[-CH_2-]$; in these works only

376   SOKOŁOWSKI AND BURCZYK

simple models of the additive contribution of the individual groupings were used which led only to the averaged values of $\Delta G°[-CH_2-]$.

In order to compare directly these averaged values of $\Delta G°_{\pi=const.}[-CH_2-]$ for compounds (I) and (II) we have assumed a simplified additive model of adsorption of monoethers (I) (as compared with Eq. [4], in which the term $b_3 \cdot n \cdot z$ has been omitted). The so-averaged values of $\Delta G°_\pi[-CH_2-]$ of monoethers (I) for all the presented values of π shown in Table VI are slightly less negative than those for alcohols (II) (cf. Table IV). These values are convergent with an increase in π, and at $\pi = 20$ mN m^{-1} they are -1.07 (±0.02) and -1.29 (±0.04) RT, respectively. This fact of convergence of the values of $\Delta G°_\pi[-CH_2-]$ for monoethers (I) and alcohols (II) has also been observed by other workers. Thus, Kurzendörfer and Lange (19) have observed that straight lines expressing the log c vs C_n relationship for aliphatic alcohols and monoethers of polyoxyethylene glycol at a constant value of the decrease in surface tension equal to $\pi \sim 33$ mN m^{-1} have a similar slope. The data reported in this work indicate that the straight lines cross each other at C_7 on the abscissa. Unfortunately, the statistical verification of the slope

of these lines has not been given and, hence, it is not possible to conclude unequivocally whether the increments $\Delta G°_\pi[-CH_2-]$ at $\pi \sim 33$ mN m^{-1} differ for both these groups of compounds or not.

The negative values of averaged increment $\Delta G°_\pi[-OCH_2CH_2-]$ (cf. Table VI) indicate an increasing effective length of the hydrocarbon chain in monoethers (I) affected by an oxyethylene grouping. $\Delta G°_\pi[-OCH_2CH_2-]$ attains the highest absolute values at low degrees of coverage of the surface, then its absolute values decrease with an increase in π and at the neighbourhood of CMC $\Delta G°_{CMC}$ $[-OCH_2CH_2-]$ approaches zero (11).

The values of b_0 presented in Tables III and IV, calculated from the regression equations for the compounds (I) and (II), were used for calculating the increments $\Delta G°_\pi[-OH]$. From studies of the solubilities of liquid alkanes in water at 298°K (20-23) comes the relation:

$$\Delta G°[CH_3-] = \Delta G°[-CH_2-] - 2.244\ RT. \quad [8]$$

Therefore, a value of b_0 can be considered as a sum of two components: (i) the increment $\Delta G°[-OH]$ and (ii) the difference $\Delta G°[-CH_2-] - \Delta G°[CH_3-]$, or

$$\Delta G°[-OH] = b_0 + 2.244\ RT. \quad [9]$$

TABLE VI

Regressions of Values of the Standard Free Energy of Adsorption for Monoethers (I) at the Aqueous Solution-Air Interface, Eq. [4], without product $b_3 \cdot n \cdot z$

Equation: π [mN m^{-1}]:	[4o] 0	[4p] 1	[4r] 5	[4s] 10	[4t] 15	[4u] 20
			Regression coefficients			
$b_0{}^a$	−7.731	−6.464	−4.892	−3.713	−2.813	−2.042
$S(b_0)$	(0.210)	(0.180)	(0.156)	(0.153)	(0.158)	(0.170)
b_1	−0.7166	−0.7956	−0.8939	−0.9678	−1.0234	−1.0725
$S(b_1)$	(0.0296)	(0.0254)	(0.0221)	(0.0215)	(0.0223)	(0.0241)
b_2	−0.7492	−0.6365	−0.4983	−0.3940	−0.3140	−0.2475
$S(b_2)$	(0.0308)	(0.0264)	(0.0229)	(0.0224)	(0.0232)	(0.0259)
R	0.990	0.993	0.995	0.995	0.995	0.995

Note. $Y = \Delta G°_{\pi=const.}$, $[RT]$; $N - K - 1 = 20$; $t_{\pi=0.05} = 2.086$.
$^a b_0 = \Delta G°_\pi[-OH] - 2.244\ RT$; $b_1 = \Delta G°_\pi[-CH_2-]$; $b_2 = \Delta G°_\pi[-OCH_2CH_2-]$.

ENERGY OF ADSORPTION OF NONIONICS   377

The calculated $\Delta G_\pi^\circ[-OH]$ values were for monoethers (I): − 3.52, −1.94, −0.74, +0.18, +0.96 RT, and for the primary alcohols (II): −1.83, −0.67, +0.21, +0.88, +1.47 RT for the decrease in surface tension, $\pi \approx$ 1, 5, 10, 15, and 20 mN m^{-1}, respectively. A good agreement was found between the calculated $\Delta G_{\pi=0}^\circ[-OH]$ value for alcohols with the value obtained from the data given by Aveyard and Chapman (24) (the values of $\Delta G_{c=0}^\circ$ for C_4H_9OH and $C_7H_{15}OH$ lead to $\Delta G_{c=0}^\circ[-OH] = -3.13 RT$ after applying Eq. [8]). The positive values $\Delta G_\pi^\circ[-OH]$ at fairly large π show that the typical hydrophilic effect of the -OH group can be noted only at a fairly large degree of coverage of the surface. The differences of the increments $\Delta\Delta G_\pi^\circ[-OH]$ for compounds (I) and (II) are −1.7, −1.3, −1.0, −0.7, and −0.5 RT for π = 1, 5, 10, 15, and 20 mN m^{-1}, respectively. The lower values of $\Delta G^\circ[-OH]$ for monoethers (I) than those for alcohols (II) may suggest that the -OH group situated at an end of a polyoxyethylene chain is probably less hydrated in the adsorption layer, thus it exhibits a weaker hydrophilic character. This is a very important effect which may be explained by the formation of intramolecular interactions of the hydrogen bond type, between the hydroxyl group and the oxygen atoms in the polyoxyethylene chain in the adsorption layer. Such interactions in polyoxyethylene glycol molecules and their ethers have been shown by Langbein (25) and Yamaguchi et al. (26) as cited by Manabe et al. (9). At high degrees of coverage of the surface, the presence of intermolecular hydrogen bonds between monoether molecules cannot be excluded as well. The relative acidities of the monoethers are higher than that of water (27), thus they can compete with water molecules in the formation of hydrogen bonds with the oxygen atoms of polyoxyethylene chains.

In order to illustrate the effect of differences in the hydrophilicity of hydroxyl groups and the hydrophobicity of -CH$_2$- groups in the alkyl radicals of monoethers (I) and al-

cohols (II) we used an approach presented by Manabe et al. (9), who studied the standard free energy of transition of the mentioned compounds from aqueous to organic phase. Thus we have calculated the hypothetical values of standard free energy of adsorption, $\Delta G_\pi^\circ\langle ROH\rangle$, of the monoethers $R(OCH_2CH_2)_zOH$ (I) assuming $z = 0$, by using the regression equation [4] (cf. Table III):

$$\Delta G_\pi^\circ\langle ROH\rangle$$

$$= \Delta G_\pi[R(OCH_2CH_2)_zOH]_{z=0}. \quad [10]$$

The so-calculated values of $\Delta G_\pi^\circ\langle ROH\rangle$ of the monoethers (I) were compared with the values of $\Delta G_\pi^\circ[ROH]$ for alcohols (II) having the same alkyl radicals. These values are listed in Table VII. The lower hydrophilicity of the hydroxyl group, despite the lower hydrophobicity of the -CH$_2$- groups in monoethers (I) as compared to alcohols (II), resulted in the hypothetical values of $\Delta G_\pi^\circ\langle ROH\rangle$ for butyl and amyl monoethers being more negative than $\Delta G_\pi^\circ[ROH]$ for butyl and amyl alcohols. The hypothetical monoethers without oxyethylene grouping are thus more hydrophobic than their corresponding alcohols. This conclusion confirms the notion of Manabe et al. (9) who investigated compounds (I) and (II) having short alkyl chains. The lower hydrophobicity of methylene groups of monoethers (I) as compared with that for alcohols (II) brought about an equalization of the mutual hydro-

TABLE VII

Values of $\Delta G_\pi^\circ\langle ROH\rangle$ and $\Delta G_\pi^\circ[ROH]$

Mono-ethers (I)		$\pi = 0$		$\pi = 20$ [mN m^{-1}]	
n	z	$\Delta G_\pi^\circ\langle ROH\rangle$ [RT]	$\Delta G_\pi^\circ[ROH]$ [RT]	$\Delta G_\pi^\circ\langle ROH\rangle$ [RT]	$\Delta G_\pi^\circ[ROH]$ [RT]
4	1–5	−10.4	−9.5	−6.1	−5.9
5	1–5	−11.2	−10.7	−7.3	−7.2
6	1–5	−12.1	−11.8	−8.5	−8.5
7	1–4	−12.9	−12.9	−9.7	−9.8
8	1–4	−13.7	−14.1	−10.9	−11.1

378   SOKOLOWSKI AND BURCZYK

phobic character of both these groups of compounds containing alkyl chains longer than C_6.

In order to make it possible to calculate the change of standard free energy of adsorption, ΔG_π°, from surface tension measurements on aqueous solutions of the compounds studied by using only one regression equation we propose:

$$\Delta G_\pi^\circ = b_0 + b_1 \cdot n + b_2 \cdot z + b_3 \cdot n \cdot z + b_4 \cdot \pi$$

$$+ b_5 \cdot \pi^{1/2} + b_6 \cdot n \cdot \pi + b_7 \cdot n \cdot \pi^{1/2}$$

$$+ b_8 \cdot z \cdot \pi + b_9 \cdot z \cdot \pi^{1/2} + b_{10} \cdot n \cdot z \cdot \pi$$

$$+ b_{11} \cdot n \cdot z \cdot \pi^{1/2} \quad [11]$$

where the symbols have the same meaning as in Eq. [4] (the range of π from 0 to 20 mN m^{-1}). The results of regression analysis are shown in Table VIII. Column 11a corresponds to monoethers (I) and 11b to alcohols (II). In both cases high correlation coefficients, R, justify the form of Eq. [11]. The statistical analysis made it possible to elucidate whether or not a superimposed interaction between methylene and oxyethylene

TABLE VIII

Multiple Regressions of Values of the Standard Free Energy of Adsorption, ΔG_π°, [RT]; π from 0 to 20 mN m^{-1}

Compound: Equation:	Monoethers (I) [11a]	Alcohols (II) [11b]
b_0	−7.014	−5.028
$S(b_0)$	(0.14)	(0.12)
b_1	−0.8418	−1.1297
$S(b_1)$	(0.022)	(0.019)
b_2	−1.0106	—
$S(b_2)$	(0.038)	—
b_3	0.0464	—
$S(b_3)$	(0.006)	—
b_5	1.2716	0.9481
$S(b_5)$	(0.035)	(0.040)
b_7	−0.0795	−0.0346
$S(b_7)$	(0.005)	(0.006)
b_9	0.1122	—
$S(b_9)$	(0.005)	—
R	0.998	0.999

groups and the decrease in surface tension is significant. At the final significance level $\alpha = 0.05$ the terms $b_{10} \cdot n \cdot z \cdot \pi$ and $b_{11} \cdot n \cdot z \cdot \pi^{1/2}$ were found insignificant.

The statistical approach presented in this work may make possible a better understanding of the effect of the individual structural elements of surfactants on their adsorption as characterized by the value of ΔG_π°.

APPENDIX

The regression coefficients, b_i, and their standard errors, $S(b_i)$, in Eq. [4] were estimated by the regression analysis. The multiple correlation coefficients, R, were calculated as well. The t statistics for the regression coefficients, $t(b_i)$, were calculated according to Eq. [12]

$$t(b_i) = \frac{b_i}{S(b_i)} \quad [12]$$

and the coefficients which do not fulfill the following relationship:

$$|t(b_i)| > t_\alpha \quad [13]$$

[t_α = Student's t distribution value at the assumed significance level ($\alpha = 0.05$) for $N - K - 1$ degrees of freedom (N = total number of data points)] were rejected (28).

The regression model given by Eq. [11] is obtained by use of the program "regr" (procedure maxstepregr) (29) run on the Odra 1204 computer.

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ENERGY OF ADSORPTION OF NONIONICS 379

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